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15. Seasonal dynamics of the inorganic nutrients from aquatic complex Somova-Parcheș in 2016

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Abstract: The existence of nitrogen compounds influence variety, abundance and nutritional value of aquatic organisms.
This study aimes to analyze the dynamic of nutrient inorganic forms in spring (March), summer (July) and autumn (September) seasons, in 2016. The selected sampling points were: Somova-Parcheş complex inlet (S1), Somova-Parches complex outlet channel into the Danube River (S2), rainwater and cooling water discharge from the industrial zone of Tulcea (S3), Casla lake (S4), Somova lake (S5), Parches lake (S6), Rotundu lake (S6).
Study results show that the physico-chemical characteristics and surface water quality from the aquatic complex Somova-Parches are determined by natural factors (climate, flowing regime) and also by the effects of industrial activities of Tulcea town.
Also, it were identified exceedings of maximum allowed concentrations for good ecological status, established by the Water Framework Directive transposed into Romanian legislation through MMGA Order 161/2006.

Keywords: predeltaic area, nutrients, surface water

INTRODUCTION

Nitrogen always occurs the aquatic ecosystems and often in a gaseous form. Relatively small amounts exist in the combined form of ammonium, nitrite, nitrate, urea and dissolved organic compounds of which, the nitrate is usually the most important (Mason, 2001).
The existence of nitrogen compounds influence the variety, abundance and nutritional value of aquatic organisms. Nitrogen is often present in amounts that can limit plant growth. This condition is common in warm climates, where phosphorus and silicon are present in relatively large amounts due to natural erosion or pollution. The concentration of most nitrogen compounds in lakes and rivers waters tend to follow a certain seasonal pattern (Windolf et al, 1996). Biological absorption decreases the concentrations in spring season in the photic area. During autumn and winter seasons the releases from sediment and also the precipitations, increase the nitrates concentrations and sometimes ammonium concentrations (Neniţescu, 1963).
In contrast to nitrogen, oxygen and hydrogen, of which reserve funds are in the atmosphere, phosphorus reserve fund is in the lithosphere. The decomposition and washed rocks phosphorus is released to biocenoses in terrestrial ecosystems. Absorbed by the plants, phosphorus is a part of macroenergetic compounds and nucleic acids, with an important role in energy and information transfer in living systems (Lombardo, 2006).
Through trophic chains, phosphorus compounds are transferred to consumers and decomposers. Phosphorus, taken up by primary producers from soil or water, usually in the form of ions (generally, orthophosphates) is incorporated into organic matter, it follows the food chains and than is released by decomposers and comes back into the soil or water (Wang and Li, 2010)

MATERIALS AND METHODS

Study area

For seasonal dynamic of nutrients inorganic forms in 2016, Somova-Parches aquatic complex, situated in the predeltaic area of the Danube Delta, was selected; the sampling points were: Somova-

Parches complex inlet (station 1), Somova-Parches complex outlet channel into the Danube River (station 2), rainwater and cooling water discharge from the industrial zone of Tulcea (station 3), Casla lake (station 4), Somova lake (station 5), Parches lake (station 6), Rotundu lake (station 7).

Figure 1 Map of the sampling points

Surface water samples were collected and analyzed in the spring (March), summer (July) and autumn (September) seasons, in 2016.

From the physico-chemical indicators, provided by the Romanian Order 161/2006 (****, 2006) concerning the classification of surface water quality to determine the ecological status of water bodies, Table 6, Annex C, Elements and quality standards of chemical and physico-chemical, for this study, in the selected area, were monitored:
• oxygen regime - oxygen dissolved, I_{KMnO4}.
• nutrients – ammonium-nitrogen (NH_4^+-N), nitrite-nitrogen (NO_2-N), nitrate-nitrogen (NO_3-N), dissolved phosphorus

The charts have been done based on the values obtained for each indicator (I_{KMnO4}, dissolved oxygen, N-NH_4, N-NO_2, N-NO_3, P-PO_4) in every sampling point, in each season (spring, summer, autumn).
The methodology of sampling and preservation of water samples

Each sample is considered to be representative for water quality only in the moment and in the point that it was sampled. Water samples were collected and preserved according to the current legislation. (*****, 2002[b])

For dissolved oxygen determination, water samples were preserved with specific reagents 1 ml of manganese sulfate and 2 ml of alkaline reagent per 100 ml water sample (*****, 2000[b]).
Preservation of surface water sample to determine the permanganate index is made with 5 ml H_2SO_4 7.5 mole/L for 1 liter of sample (*****, 2001 [b]).

As ISO standards recommands the nutrients determination must be carried out as soon as possible, maximum 24 hours from sampling, conserved by keeping them at 2-5^0 C. If the determination is not possible in 24 hours, 1 ml of chloroform should be added to 500 ml water sample and then kept it cool until the determination (*****, 2000[a], *****, 2001[a], *****, 2002[a], *****, 2005).

METHODS

Volumetric methods
Volumetric method covers all the methods for determining the content of a solution component by measuring the volume of titrated reactive solution with the determined substance that reacts quantitatively. By this method was determined, the dissolved oxygen and the rate of permanganate. (Pietrzyk and Frank, 1989)

Molecular absorption spectrometry methods
Molecular absorbtion spectrophotometry is one of the first method occurred and commonly used in chemical analysis laboratories and is based on the absorption of light in visible range (VIS). The

method measures the light transmitted by a colored solution, filtered through small area optical fibers, which allows a more precisely set up of the wavelength. It can be drawn a calibration curve, obtained by measuring the signal depending on the wavelength of the incident radiation (Pietrzyk and Frank, 1989). The indicators analyzed through this method are: $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$.

RESULTS AND DISCUTIONS

Oxygen regime
Permanganate index
Oxidising substances in water or chemical oxygen demand (COD) are substances that can be oxidized both at cold and temperature under the action of an oxidant (potassium permanganate or potassium dichromate). Oxidability represent oxygen amount equivalent to oxidant consumption. The organic substances are oxidized at temperature, despite the inorganic substances oxidized at cold. Manescu et al., 1994

Increasing the amount of organic substances in water or their occurrence in a specific time is synonymous with water pollution by germs, which typically accompany organic substances. Manescu et al., 1994

The organic substances in water are coming from the death of vegetable and animals organisms, the industrial wastewater, agricultural and wastewaters. The organic substances dissolved in water are present in the form of proteins, aminoacids, lipids, carbohydrates, vitamins, enzymes.
The maximum allowed concentration of permanganate index corresponding to the second quality class in accordance with Romanian Order 161/2006, is 10 mg O_2/L.

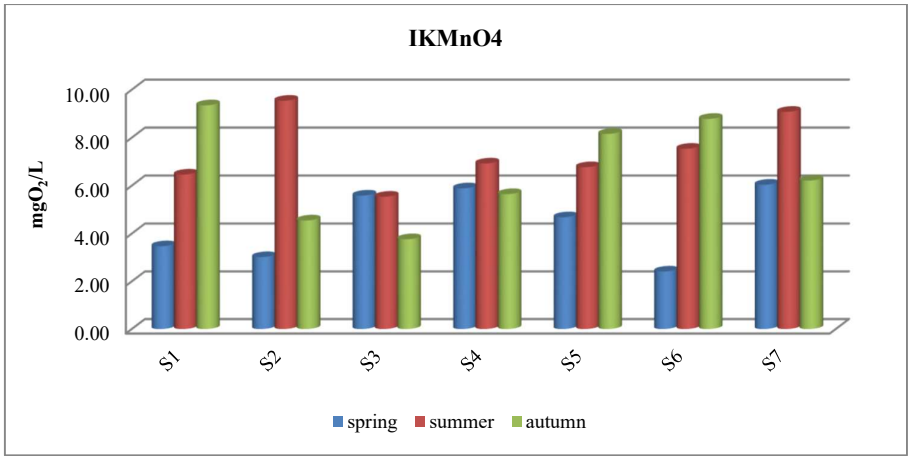

Figure 2 Seasonal evolution of I_{KMnO4}

As it can be seen in the Figure 2, the permanganate index recorded the lowest value in the spring season, due to low temperatures, expecting that increasing temperature and hence the microorganisms activities in the water, to increase the amount of organic substances, normally reaching the maximum level in summer, respectively maximum temperatures, followed by a decline of values in autumn.

In this situation are the sampling points Somova-Parches complex outlet channel into the Danube River (S2), rainwater and cooling water discharge from the industrial zone of Tulcea (S3), Casla lake, (S4) and Round lake (S7). Exceptions are S1 (Somova-Parcheş complex inlet, S5 (Somova lake) and S6 (Parches lake) sampling points, which recorded higher values in autumn, probably due to high temperatures in autumn this year, (on 4 October 2016 the samples were collected when the temperature registered 19.9^0 C), but also due to the low level of the Danube.

All permanganate index values frame into the first quality class, respectively very good ecological status, the maximum value was recorded in Somova-Parches complex outlet channel into the Danube River (S2), 9.538 mg O_2/L, in summer and minimum value (2.415 mg O_2 /L) in Parches lake (S6) in spring season.

Dissolved oxygen
Dissolved oxygen in water is one of the most important biogenic factors. Aerobic organisms take the dissolved oxygen from the atmosphere and those living in water find it dissolved, coming from oxygen developed during chlorophyll assimilation of submerged plants and later developed in water. It determines not only the fish life, but also the mineralization of organic substances that can be assimilated by plants only as inorganic form. Mason, 2001
Disolved oxygen solubility increases with temperature decreasing, recording highest values in the cold season when the temperature is lower. Manescu et al., 1994
The maximum allowed concentration for dissolved oxygen, corresponding to the second quality class, in accordance with Romanian Order 161/2006, is 7 mg O_2 /L.

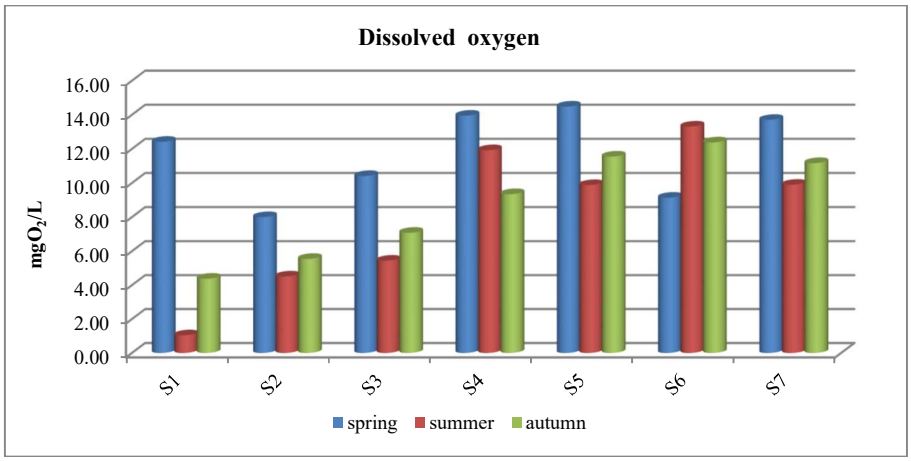

Figure 3 Seasonal evolution of Dissolved oxygen

Analyzing the values of dissolved oxygen (Figure 3), aquatic complex Somova-Parches is in a good correlation with temperature, in the sampling points Somova-Parches complex inlet (S1), Somova-Parches complex outlet channel into the Danube River (S2), rainwater and cooling water discharge from the industrial zone of Tulcea (S3), lake Somova (S5), lake Round (S7), the highest values recorded in the spring season, followed by a decreasing in summer when the temperature is higher then those recording an increasing in autumn. The explanation for this behavior is the fact that an increased temperature leads to lower oxygen solubility.

This rule is not applied for lakes Casla and Parches (S4 and S6 sampling points), where higher values were recorded in summer; similar to permanganate index, an explanation could be that this year autumn temperatures were very high (19.9^0 C on 4 October when samples were collected), and also the fact that this zone is influenced by the industrial area.

The maximum recorded concentration of dissolved oxygen, in 2016, was in Somova Lake (S5 sampling point) 14.488 mg O_2 /L in the spring season and the minimum concentration 1.042 mg O_2 /L, in Somova-Parches complex inlet (S1 sampling point), in summer; this concentration was recorded, probably, due to the low level of the Danube.

Ammonium-Nitrogen
Ammonia results in water from incomplete decay of organic substances containing nitrogen, or can come also from soil. It is the first stage of the decomposition of organic substances containing nitrogen in their molecule, and therefore indicates a recent pollution (hours, days), therefore very dangerous. Mason, 2001
The maximum allowed concentration for $N\text{-}NH_4$ corresponding to the second quality class in accordance with Romanian Order 161/2006, is 0.8 mg N/L.

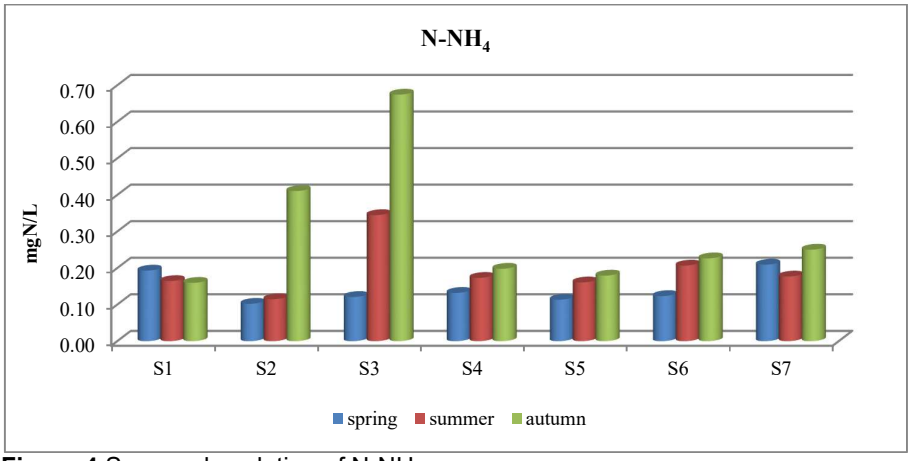

Figure 4 Seasonal evolution of $N\text{-}NH_4$

Analyzing the data from the Figure 4, it can be observed that the lowest concentrations of ammonium nitrogen is registred in spring, followed by an increase of its levels in summer and autumn seasons, except for the sampling point S1 (Somova-Parches complex inlet). The maximum value was recorded in the sampling point S3 (rainwater and cooling water discharge from the industrial zone of Tulcea) in autumn, 0.647 mg $N\text{-}NH_4$/L, this value framed into the second quality class, good environmental status. The minimum value, 0.102 mg $N\text{-}NH_4$/L, was recorded in S2 sampling point (Somova-Parches complex outlet channel into the Danube River), in spring season.

Nitrites
Nitrites come in water from the mineralization of organic substances under the action of bacteria. Nitrites cause a deoxygenation of water by using existing oxygen, which causes their trasformations into nitrates. Nitric form of nitrogen is the most assimilable. Mason, 2001

The maximum allowed concentration of nitrite nitrogen, corresponding to the second quality class, in accordance with Romanian Order 161/2006, is 0.03 mg $N\text{-}NO_2$/L.

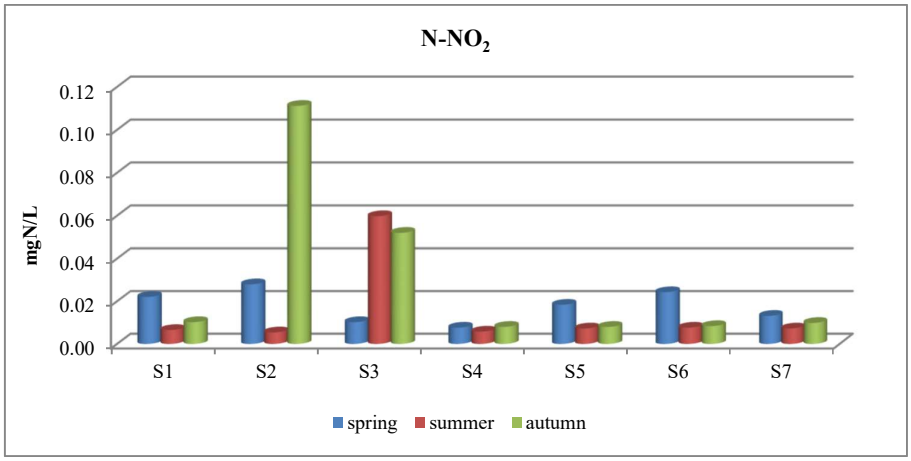

Figure 5 Seasonal evolution of $N\text{-}NO_2$

As it is shown in Figure 5, the highest values were recorded in the spring season, except for the sampling points Somova-Parches complex outlet channel into the Danube River (S2) and rainwater and cooling water discharge from the industrial zone of Tulcea (S3), this sampling points being influenced by the discharge of the industrial area; a decreasing of levels in summer followed by an increasing in autumn were observed.

Seasonal variation of nitrite-nitrogen from generally ranged between 0.005 and 0.024 mg $N\text{-}NO_2$/L, framing into the first and second quality classes, respectively very good and good ecological status.

The exception is S2 sampling point (Somova-Parches complex outlet channel into the Danube River), which recorded, as in the case of ammonium-nitrogen, the maximum concentration in autumn season (0.111 mg $N\text{-}NO_2$/L), and S3 sampling point (rainwater and cooling water discharge from the industrial zone of Tulcea) in autumn and summer seasons (0.050 and 0.052 $N\text{-}NO_2$/L), exceeding the second quality class, moderate ecological status.

Nitrates
The final form of organic nitrogen oxidation in water is nitrates. The presence of nitrates in surface waters is mainly determined by the contact with hidrografic basin soil. The nitrates concentrations in surface water varie with temperature, dissolved oxygen concentrations, the presence of organic substaces and pH. Under the action of microorganisms, nitrates are reduced to nitrogen compounds poor or without oxygen. Mason, 2001
The maximum allowed concentration of $N\text{-}NO_3$ corresponding to the second quality class in accordance with Romanian Order 161/2006, is 3 mg $N\text{-}NO_3$ /L.

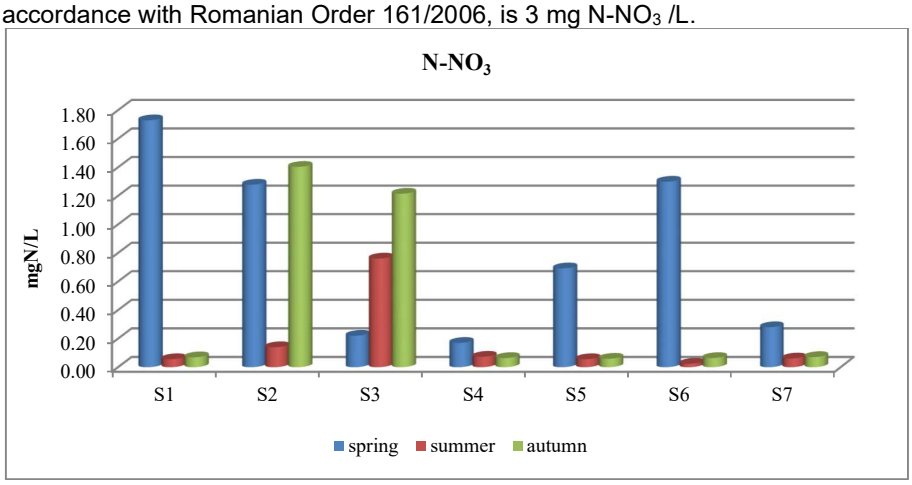

Figure 6 Seasonal evolution of $N\text{-}NO_3$

The results showed that the highest values of nitrates were recorded in spring season, nitrates varie with temperature and dissolved oxygen; at low temperature and high levels of dissolved oxygen, nitrate concentration increases, nitrates being the most stable form of nitrogen compounds. Minimum concentrations were recorded in summer season, at maximum temperatures, low oxygen concentrations and high amounts of organic substances, followed by a increasing in autumn season. Exceptions to this rule are S2 sampling point (Somova-Parches complex outlet channel into the Danube River), which recorded the highest value in autumn (as in the case of the others forms of nitrogen (ammonium, nitrites)), S3 sampling point (rainwater and cooling water discharge from the industrial zone of Tulcea), which recorded values inversely propotional with the normal variation of nitrates, because of the high water temperature from industrial area.

The maximum concentration of nitrates was recorded in spring season in the sampling point Somova-Parches complex inlet (S1), 1.729 mg $N\text{-}NO_3$/L, the minimum concentration was recorded in summer in Parches lake (S6), 0.024 mg $N\text{-}NO_3$/L. All concentrations framed into the first and second quality classes, respectively very good and good ecological status.

Phosphates
Phosphorus is a biogenic element, used by bacteria and plants to produce primary production and is often absent in water during the summer. In winter, phosphates reserve is recovered due to phosphorus transition in mineral phosphorus, from dead organisms. Mason, 2001
Phosphates come in water from pollution with industrial wastewaters, pesticides, fertilizers and detergents. It favors natural basins eutrophication through their role in algae development.
The maximum allowed concentration of $P\text{-}PO_4$, corresponding to the second quality class in accordance with Romanian Order 161/2006, is 0.2 mg $P\text{-}PO_4$/L.

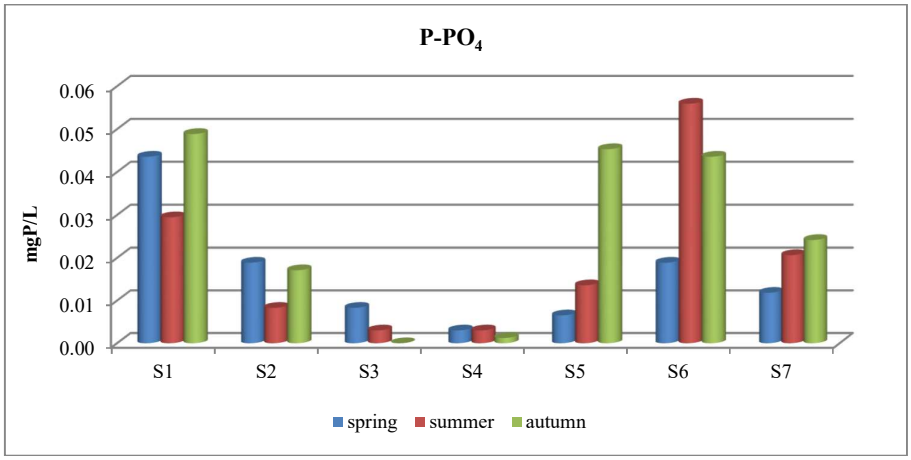

Figure 7 Seasonal evolution of P-PO_4

Analyzing the obtained data (Figure 7), significant differences in seasonal dynamic of orthophosphates in Somova-Parches aquatic complex were observed.

A seasonal variation trend of mineral phosphorus was noticed, generally with maximum levels in autumn (in September), values that can be attributed to weather phenomena, respectively the rains during the sampling, which train the bottom sediment, causing the increasing of the mineral phosphorus concentrations. Values ranged between 0.03 and 0.056 mg P-PO_4/L and it can be observed that Casla lake (S4) is strongly influenced by the discharging from the industrial area, because of the cooling water temperature. An exception is the sampling point S6 (Parches lake), which recorded the maximum level in summer (0.056 mg P-PO_4/L), this being the maximum recorded value of the orthophosphates.

The maximum allowed concentration of 0.02 mg P-PO_4/L for orthophosphates was not exceeded in any sampling point from the studied aquatic complex, the values framing into the first quality class (in accordance with Romanian Order 161/2006), respectively very good ecological status.
Based on the results we can conclude that the nutrients concentrations in deltaic ecosystems are the result of the relatively low consumption of nutrients by phytoplankton and aquatic plants, inhabiting surface waters in the spring season; the results are in accordance with the literature (study made by Athuman C. B., 2012)

CONCLUSIONS

The physico-chemical characteristics and surface water quality of the Danube Delta Biosphere Reserve are determined by natural factors (natural frame, climate, flowing regime) and by various economic activity in adjacent area. In the predeltaic area, changes can be influenced by the effects of the industrial activities of Tulcea town.

Generally, the values for the studied indicators, framed into the first and second quality class, respectively very good and good ecological status (except for dissolved oxygen, which framed in the third and fourth quality class and nitrites, which framed in the third quality class).

AKNOLEDGMENTS

This study was supported by Ministry of Education and Research within Nucleus Program 16 28 01 04 “Assessment of ecological status in aquatic ecosystems in the Danube Delta Biosphere Reserve in 2015”, Contract no. 47N/2016_Danube Delta.

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Received 11 March 2017
Revised 12 April 2017